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Research papers

Using stable isotopes and tritium to delineate groundwater flow systems and their relationship to streams in the Geum River basin, Korea

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ABSTRACT

This study aims to clarify groundwater and stream water flow systems in the Geum River basin, Korea, which is an area with a crystalline basement using $\delta^{18}O$, $\delta^{2}H$, and ^{3}H. Stable isotopes of precipitation showed clear differences between dry and rainy seasons due to the Asian monsoon. Groundwater and stream water samples were collected in the dry and rainy seasons in three hydrographic zones of the upper, middle, and lower zones. The contribution of rainy season precipitation to groundwater recharge based on deuterium excess was 71–89%, far exceeding the amount fraction of the season in total precipitation. Stable isotopic compositions of groundwater and stream water showed little seasonal variation, and indicated the dominance of high-altitude recharge in the upper zone. Groundwater with lower ^{3}H was mainly observed in that area, indicating a contribution of intermediate flow with a longer residence time. In contrast, stream water and some groundwater samples in the lower zone showed seasonal variability and signatures of 10–20% evaporation in their stable isotopic composition. The ^{3}H content of groundwater in the lower zone was high, indicating that the local flow system is dominant. These regional features also influenced the relative contributions of rainy season precipitation, dry season precipitation, and local recharge with evaporation signature, as estimated from $\delta^{18}O$ and deuterium excess values, and ^{3}H in groundwater. Stream water from lower-order streams of the river had stable isotopic compositions similar to those in the upper zone, indicating a considerable contribution of groundwater discharge in the mountainous areas to the lower reach of the river. These results have implications for sustainable management of water resources in the basin during predicted changes in water usage and precipitation patterns due to climate change, as well as in regions with similar climatic and hydrologic conditions.

1. Introduction

Understanding water flow systems at the regional scale is critically important for management of water resources (Banks et al., 2011; Genereux et al., 2013). The stable isotopes of water are widely used as natural tracers to elucidate hydrogeological processes at various scales and sustainably maintain and manage water resources (Abbott et al., 2000; Kortelainen and Karhu, 2004; McGuire and McDonnell, 2006; Kabeya et al., 2007; Beisner et al., 2018; Rey et al., 2018). Since Tóth (1963) first proposed a conceptual model of groundwater flow divided into local, intermediate, and regional groundwater flow in hypothetical homogeneous and isotropic drainage basins, several studies have attempted to characterize water flow processes by developing various environmental tracers and hydrogeochemical parameters (Paternoster et al., 2008; Wassenaar et al., 2011; Liu and Yamanaka, 2012; Jódar et al., 2016; Panda et al., 2018; Rey et al., 2018), often associated with distribution of fracture zones and faults to identify groundwater flow paths (Pacheco and Van der Weijden, 2014a,b; Pacheco, 2015).

Numerous studies have been conducted to clarify groundwater flow systems using conceptual models associated with various hydrological and structural settings based on stable isotopes. James et al. (2000) used multi-isotopic tracers to demonstrate that the Lower Opal Springs and Spring River were controlled by mixing processes of local and regional groundwater flow, while the regional flow system was

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influenced mainly by the Metolius River in the central Oregon Cascades. Kim and Jeong (2005) found that natural occurrence of fluoride-rich groundwater was associated with the hydrologic conditions of a fault zone using the relationship between stable isotope and fluoride concentrations. Tsujimura et al. (2007) successfully identified interactions between groundwater and river water in a stream network using a multi-tracer approach. Pacheco and Van der Weijden (2014a) used $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ to estimate depth of water circulation in a small watershed. Peng et al. (2018) evaluated the recharge processes of montane water and their importance to adjacent valley-plain groundwater in a tectonic suture zone using natural-tracer-based end-member mixing analysis (EMMA).

Multiple environmental tracers provide additional information on groundwater flow systems (Maloszewski et al., 2002). In particular, environmental ^{3}H is commonly used alongside stable isotopes to trace the origin of water in the hydrological cycle. Abbott et al. (2000) revealed that the degree of mixing between local recharge and deep groundwater is temporally and spatially variable due to differences in the interconnection of bedrock fractures based on a comparison of $\delta^{18}O$ in groundwater and precipitation and groundwater age, which was determined from ^{3}H. Joshi et al. (2018) used stable isotopes and ^{3}H to identify the recharge sources of groundwater and to systematically characterize flow paths in the northwest Indian aquifer system.

Considerable research on groundwater flow systems has been conducted using environmental tracers in karst aquifers (Vandenschrick et al., 2002; Perrin et al., 2003; Zhao et al., 2018) and volcanic aquifer systems (Demlie et al., 2007; Paternoster et al., 2008; Hernández-Antonio et al., 2015), but few studies have been conducted in crystalline aquifer systems (Praamsma et al., 2009; Leketa et al., 2018; Petelet-Giraud et al., 2018). The Geum River basin in South Korea consists of high mountains in the east and plains in the west, and its major lithology is crystalline bedrock and alluvium. In 2017, annual groundwater usage in the basin was 46.8 billion tons, corresponding to 11.6% of total groundwater usage in South Korea (KOWACO, 2017). A few studies have employed environmental isotopes to characterize geothermal water systems or trace the origin of CO_2-rich water in bedrock aquifers at a local scale (Kim et al., 2000; Jeong et al., 2001; Kim et al., 2005). However, no regional studies have been carried out to delineate the groundwater flow system in the Geum River basin using environmental isotopes.

This study aims to describe the surface and groundwater flow systems in the Geum River basin using stable isotopes of $\delta^{18}O$ and $\delta^{2}H$, as well as ^{3}H. The specific objectives are to identify the factors controlling the spatial and temporal variability of stable isotopes and ^{3}H in alluvial and crystalline bedrock aquifers at the regional scale and to assess the recharge processes and flow paths of groundwater as well as stream–aquifer interactions in the basin. We also established a conceptual model of the water flow systems in the basin considering its hydrographic and hydrogeologic settings.

2. Study area

The area of the Geum River basin is around 9915 km^2 and is located in the central part of the Korean Peninsula (Fig. 1). The Geum River, one of four national rivers, has a linear length from source to mouth of about 85 km and a total length of stream channels of 396 km (KOWACO, 2002). The Geum River consists of 10 national streams, 20 first-class regional streams and, 460 s-class regional streams, and discharges into the Yellow Sea. The ten sub-basins of the Geum River watershed were classified into three hydrographic groups: upper zone (K1–K3), middle zone (K4–K6), and lower zone (K7–K10) (Table 1).

The Geum River basin consists primarily of Precambrian meta-sedimentary rocks and Jurassic/Cretaceous granitic rocks (Cheong et al., 2003). No sizeable exposures of carbonates or evaporites have been reported. Weathered zones of granitic rocks and gneiss are widely dispersed in the study area. Alluvial aquifers are present in the lower parts of the sub-basins at a thickness of 7–20 m, but are poorly developed in the upper parts of the sub-basins within mountainous areas (KOWACO, 2002). A large number of fractures with random orientations can be observed in the study area. Groundwater flow within the crystalline bedrock is controlled by structural discontinuity and the connectivity of fractures (Lee and Lee, 2000; Maréchal et al., 2004).

The monthly mean air temperature from 1981 to 2010 was 13 °C and ranged from −1.0 °C in January to 25.6 °C in August. The mean annual precipitation (1981–2010) is 1458.6 mm, around 71% of which falls during summer (June to September). Winter (December to February) is cold and dry, whereas summer (June to September) is hot and humid with frequent heavy rainfall (Lee et al., 1999). In this study, June to September were classified as rainy season, and October to May as dry season considering monthly rainfall (Lee et al., 1999). Annual precipitation is mainly controlled by the East Asian monsoon. Annual precipitation in 2017 was 1127.5 mm, approximately 77% of which occurred rainy season (KMA, 2018). The recharge rate of the Geum River basin ranged from 9.2% to 15.8% for sub-basins with an average of 13.6% and no clear trend was not observed for the three hydrographic zones (MOLIT, 2012).

The Geum River is highly regulated like other rivers in Korea and various water storage facilities has been constructed in the basin including two large dams in the upper basin, weirs, and reservoirs on the tributaries to secure water supply for drought conditions (Ahn et al., 2014). In recent years, the Four Rivers Restoration Project, launched as part of the “Green New Deal” policy in 2009 has incurred significant environmental changes in the Geum River after construction of three barrages on the mainstream (Kim et al., 2016). However, this restoration project and policy were implemented without a conceptual model of the groundwater flow system and its interaction with surface water, which has led to limitations in the understanding of regional hydrogeological processes.

3. Methods

3.1. Sample collection

A total of 195 rainfall and snowfall samples were collected weekly at three stations located at altitudes of 140, 431, and 790 m a.m.s.l. over two years from August 2014 to August 2016 at Mt. Gyeryong, which is located in the central portion of the study area. Precipitation samples were stored in 30-L plastic containers coupled with a filter mesh to prevent debris contamination, which were coated with about 250 mL of mineral oil to prevent evaporation. The mineral oil in the precipitation samples was removed using a 1-L glass separatory funnel. All precipitation samples were stored upside-down at 4 °C in 20-mL polyethylene vials with PolyCone-lined caps and Parafilm seals until analysis. Rainfall and air temperature were measured at three stations using tipping bucket rain gauges with HOBO loggers (1 pulse/0.2 mm rain; aerodynamic rain gauge; Eijkelkamp, Giesbeek, Netherlands). The loggers were programmed to record air temperature at 1-min intervals.

In total, 67 groundwater samples from 46 bedrock aquifer wells and 21 shallow aquifer wells in the National Groundwater Monitoring Network (NGMN) were collected in April and September 2017. Each NGMN site has a bedrock aquifer monitoring well with total depth of 40–150 m (avg. 76 m), and some sites also have a shallow aquifer monitoring well with total depth of 8–27 m (avg. 15 m). In addition, 67 water samples were collected from perennial streams near the groundwater monitoring sites under base flow conditions at least three days after any rainfall event to minimize the contribution of direct runoff to stream discharge. Stream order numbers based on the Strahler ordering system were assigned to the stream network (Table 2). A headwater stream with no tributaries is classified as order 1 in the Strahler ordering system, and the order increases wherever two segments of the same order meet. When two segments of unequal order meet, the highest-order number is retained (Strahler, 1957). Water

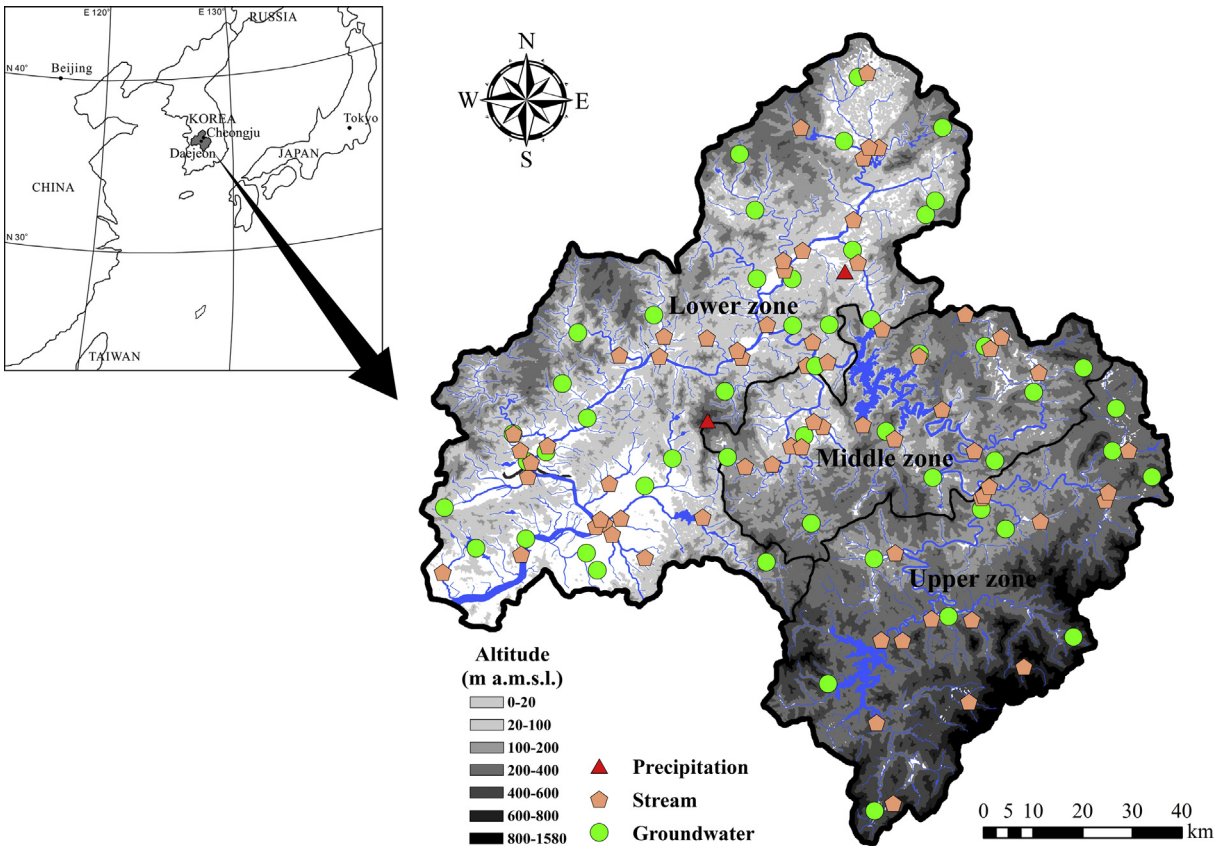

Fig. 1. Location of sampling sites in the Geum River basin, South Korea, which was divided into three hydrographic zones: upper zone, middle zone, and lower zone. Pentagons and circles denote the stream and groundwater sampling sites, respectively, and triangles denote precipitation stations at Mt. Gyeryong, with three stations along an altitude gradient (southern site) and a GNIP station at Cheongju (northern site).

temperature, electrical conductivity (EC), dissolved oxygen (DO), and pH were measured in the field using portable instruments. Water samples were filtered through 0.2-μm membrane filters in the field.

3.2. Analytical methods

The isotopic and chemical compositions of the water samples were analyzed at the Groundwater Research Center, Korea Institute of Geoscience and Mineral Resources (KIGAM; Daejeon, South Korea). The hydrogen and oxygen stable isotopic compositions of the water samples were determined through wavelength-scanned cavity ring-down spectroscopy (WS-CRDS; L2120-*i*; Picarro, Santa Clara, CA, USA), a type of isotope ratio infrared spectroscopy that is widely used in hydrologic applications (Penna et al., 2010; Liu and Yamanaka, 2012). All water samples were heated to 110 °C in a vaporizer, and then sent to the cavity of WS-CRDS under dry N_2 gas (> 99.999% purity). All isotopic ratio results are reported using δ-notation (‰) relative to the international standard VSMOW2 (Vienna Standard Mean Ocean Water 2). The primary standards VSMOW2, GISP, and SLAP2, and secondary standards were used to calibrate the stable isotopic composition and to identify day-to-day changes in analytical quality and drift effects. WS-

Table 2
Number of stream water samples corresponding to stream order numbers of the Strahler ordering system.

Hydrographic zone	First order	Second order	Third order	Fourth order	Fifth order
Total	19	17	20	6	5
Upper zone	7	2	6	1	–
Middle zone	6	6	4	1	–
Lower zone	6	9	10	4	5

Table 1
Specification of sub-basins in the Geum River basin (KOWACO, 2002) and three hydrographic zones used in this study.

Hydrographic zone	Sub-basin	Area (km^2)	Groundwater usage per unit area ($m^3/day/km^2$)	Mean altitude (m a.s.l.)	Topographic gradient (°)
Upper zone	K1	932.4	16.75	502	9.9
	K2	1163.9	47.74	400	9.8
	K3	807.8	36.24	355	8.9
Middle zone	K4	554.3	99.61	268	7.5
	K5	748.5	80.74	201	8.6
	K6	663.4	158.58	181	7.2
Lower zone	K7	1837.6	208.04	139	5.1
	K8	664	107.41	124	6.3
	K9	967.3	54.77	141	7.1
	K10	1540.8	139.49	83	4.2

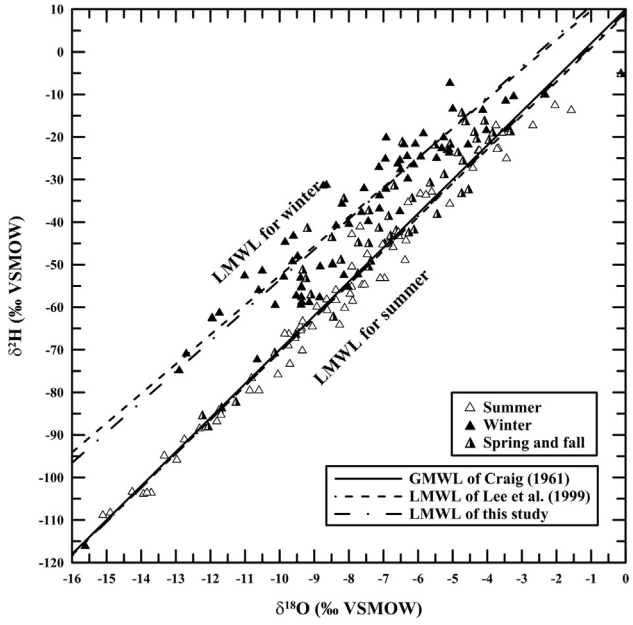

Fig. 2. Stable isotopic composition of precipitation collected at Mt. Gyeryong stations. Local meteoric water lines (LMWL) for summer and winter were constructed based on weekly measurements from the three stations at the site.

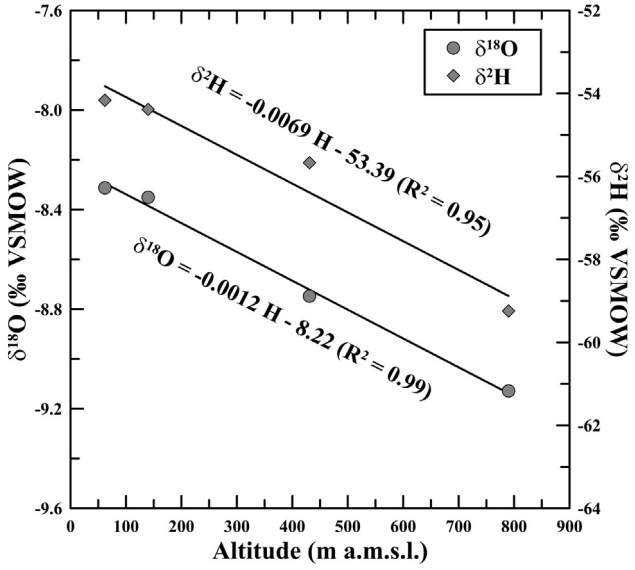

Fig. 3. Relationship between the amount-weighted mean stable isotopic composition of precipitation and altitude (m) of the three substations at Mt. Gyeryong and GNIP station at Cheongju.

CRDS has uncertainties of 0.1 and 0.5‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (Jung et al., 2013; Kim et al., 2017).

Groundwater samples collected in April were also analyzed for their ^{3}H contents. ^{3}H was analyzed using low-level liquid scintillation counting after electrolytic enrichment of the initial sample from a volume of 500 to 1000 mL at the University of Waterloo (Waterloo, ON, Canada), University of Miami (Miami, FL, USA), and KIGAM. Typical detection limits are 0.6–0.1 TU, mainly depending on the degree of electrolytic enrichment. More detailed analytical procedures were reported by Yoon et al. (2010).

4. Results

4.1. Stable isotopic composition of precipitation

The measured $\delta^{18}O$ and $\delta^{2}H$ in precipitation ranged from −15.6‰ to −0.1‰ and −116‰ to −5‰, respectively (Fig. 2). Seasonal local meteoric water lines (LMWL) were defined using these measurements, resulting in $\delta^{2}H = 7.98\ \delta^{18}O + 9.28‰$ (n = 69, $R^2 = 0.98$) for summer (June to September), and $\delta^{2}H = 7.16\ \delta^{18}O + 17.97‰$ (n = 66, $R^2 = 0.87$) for winter (November to February) precipitation and snowfall. The LMWL for summer was close to the global meteoric water line (GMWL) defined by Craig (1961), whereas the LMWL for winter was plotted to the left of the GMWL with more widely scattered data than the LMWL for summer. These two LMWLs were very similar to those defined by Lee et al. (1999) for precipitation in Daejeon and Seoul, Korea. Deuterium excess, $d = \delta^{2}H - 8{\cdot}\delta^{18}O$ (Dansgaard, 1964), ranged from −3.8‰ to 38.7‰ and the seasonal averages were 8.9 ± 3.9‰ and 23.7 ± 7.5‰ for summer and winter, respectively. Because the study area is located in East Asia, where the Asian monsoon dominates precipitation patterns, seasonally distinct d values were obtained due to the changing air masses and moisture sources (Lee et al., 2003).

Altitude effects on $\delta^{18}O$ and $\delta^{2}H$ in precipitation were determined using measurements collected at three stations in Mt. Gyeryong as well as the Cheongju station of the Global Network for Isotopes in Precipitation (GNIP) in 2015. Even though the Cheongju station is about 37 km from the stations in Mt. Gyeryong, the amount of precipitation and weighted mean stable isotopic composition of precipitation were similar during the same period. Strong correlations were observed between altitude and the mean stable isotopic composition weighted based on the amount of precipitation (Fig. 3). The isotopic lapse rate with changing altitude was calculated to be −0.12‰ per 100 m for $\delta^{18}O$ and −0.7‰ per 100 m for $\delta^{2}H$. The isotopic lapse rates in the study area were relatively small compared to the global average isotopic lapse rate of −0.28‰ per 100 m for $\delta^{18}O$ (Poage and Chamberlain, 2001), but were similar to the average lapse rate in China (Liu et al., 2014). Because the extent of the altitude effect can reflect the local climate and topography of a region, similar lapse rates have been reported in some other regions influenced by the Asian monsoon system (Machida and Shindo, 1999; Mandal et al., 2011).

In mid-latitude regions, temperature and precipitation amount are important factors controlling the final isotopic composition of precipitation (Dansgaard, 1964; Lee et al., 2003). However, their relative contributions to the isotopic fractionation of precipitation vary spatially, particularly in the Asian monsoon region (Liu et al., 2014). Because both air temperature and rainfall amount are highest in summer in this region, the effects of temperature and precipitation amount on the isotopic composition of precipitation offset each other to some extent (Johnson and Ingram, 2004). In the study area, the latitude effect was not considered as a major factor because the LMWLs in Daejeon, Seoul, and Pohang showed no significant differences (Lee and Lee, 1999). The effect of precipitation amount and the altitude effect by orographic lift are the main factors considered to influence the isotopic fractionation of precipitation in the Geum River basin. In the Mt. Gyeryong area, the amount of annual precipitation increased from 688 mm at the base to 1245 mm at the top, which could be attributed to orographic lift.

4.2. Stable isotopic composition of stream water and groundwater

The average values of $\delta^{18}O$ and $\delta^{2}H$ for stream water were −7.0‰ and −48‰ in the dry season, and −8.0‰ and −55‰ in the rainy season, respectively (Table 3). The lowest $\delta^{18}O$ and $\delta^{2}H$ values were observed in the stream network in the upper zone. Most stream water was below the LMWL in summer, indicating that stream water has undergone isotopic enrichment due to evaporation (Fig. 4). Local evaporation lines were determined using the $\delta^{18}O$ and $\delta^{2}H$ values of stream water, resulting in $\delta^{2}H = 6.4\ \delta^{18}O - 2.6‰$ (n = 67, $R^2 = 0.93$) for the dry season and $\delta^{2}H = 5.7\ \delta^{18}O - 9.0‰$ (n = 67, $R^2 = 0.87$) for the

Table 3
Stable isotopic compositions of groundwater and stream water in three hydrographic zones.

Hydrological component	Hydrographic zone	Dry season									Rainy season								
		n	Minimum		Maximum		Average		Standard deviation		n	Minimum		Maximum		Average		Standard deviation	
			$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$		$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$
Groundwater	Total	67	−9.6	−66	−6.8	−47	−8.2	−56	0.61	4.4	67	−9.6	−66	−7.0	−48	−8.3	−56	0.59	4.3
	Upper zone	13	−9.6	−66	−7.9	−52	−8.7	−59	0.45	4.2	13	−9.6	−66	−7.7	−53	−8.6	−59	0.53	4.2
	Middle zone	14	−9.4	−65	−8.1	−54	−8.6	−59	0.44	3.7	14	−9.4	−66	−8.1	−54	−8.7	−59	0.47	3.9
	Lower zone	40	−9.2	−64	−6.8	−47	−7.9	−54	0.5	3.5	40	−9.3	−63	−7.0	−48	−8.1	−55	0.53	3.6
Stream water	Total	67	−9.0	−60	−4.2	−29	−7.0	−48	1.12	7.4	67	−9.2	−62	−6.5	−46	−8.0	−55	0.49	3.0
	Upper zone	16	−9.0	−59	−7.4	−47	−8.1	−54	0.5	2.9	16	−9.2	−62	−7.7	−51	−8.3	−56	0.45	2.8
	Middle zone	17	−8.8	−60	−6.1	−39	−7.7	−52	0.63	4.8	17	−8.8	−59	−7.4	−53	−8.3	−56	0.35	1.7
	Lower zone	34	−7.8	−55	−4.2	−29	−6.2	−43	0.88	6.6	34	−8.6	−60	−6.5	−46	−7.8	−54	0.46	3.3

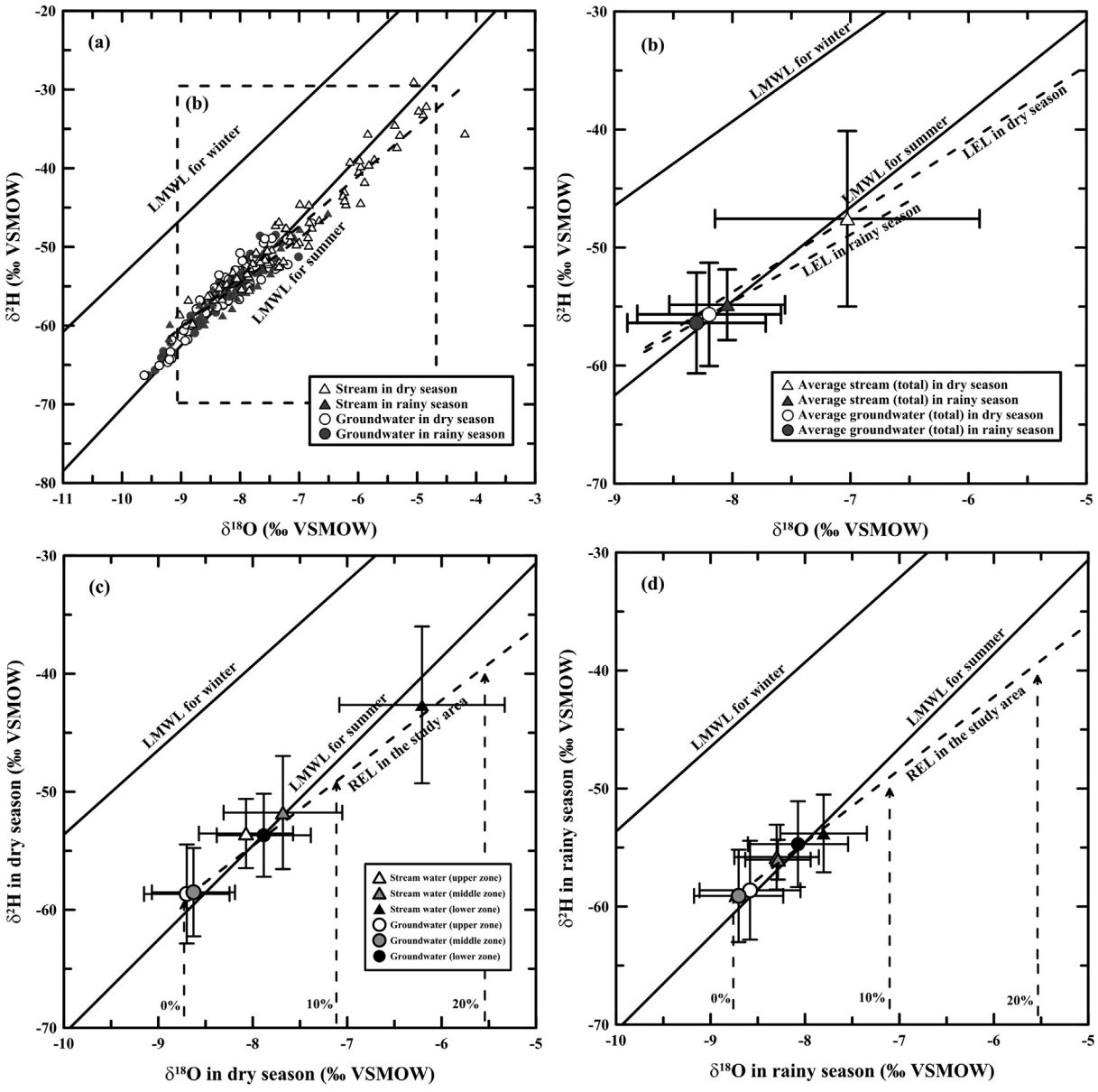

Fig. 4. Stable isotopic compositions of groundwater and stream water in the dry and rainy seasons. All measured data (a) and the average values of groundwater and stream water (b) are shown. Local evaporation lines (LEL) of stream water in the dry and rainy seasons are plotted in (b). Average values of the three hydrographic zones are shown for the dry season (c) and rainy season (d) with Rayleigh evaporation lines (REL) calculated using the average temperature and relative humidity over the last 30 years (1981–2010).

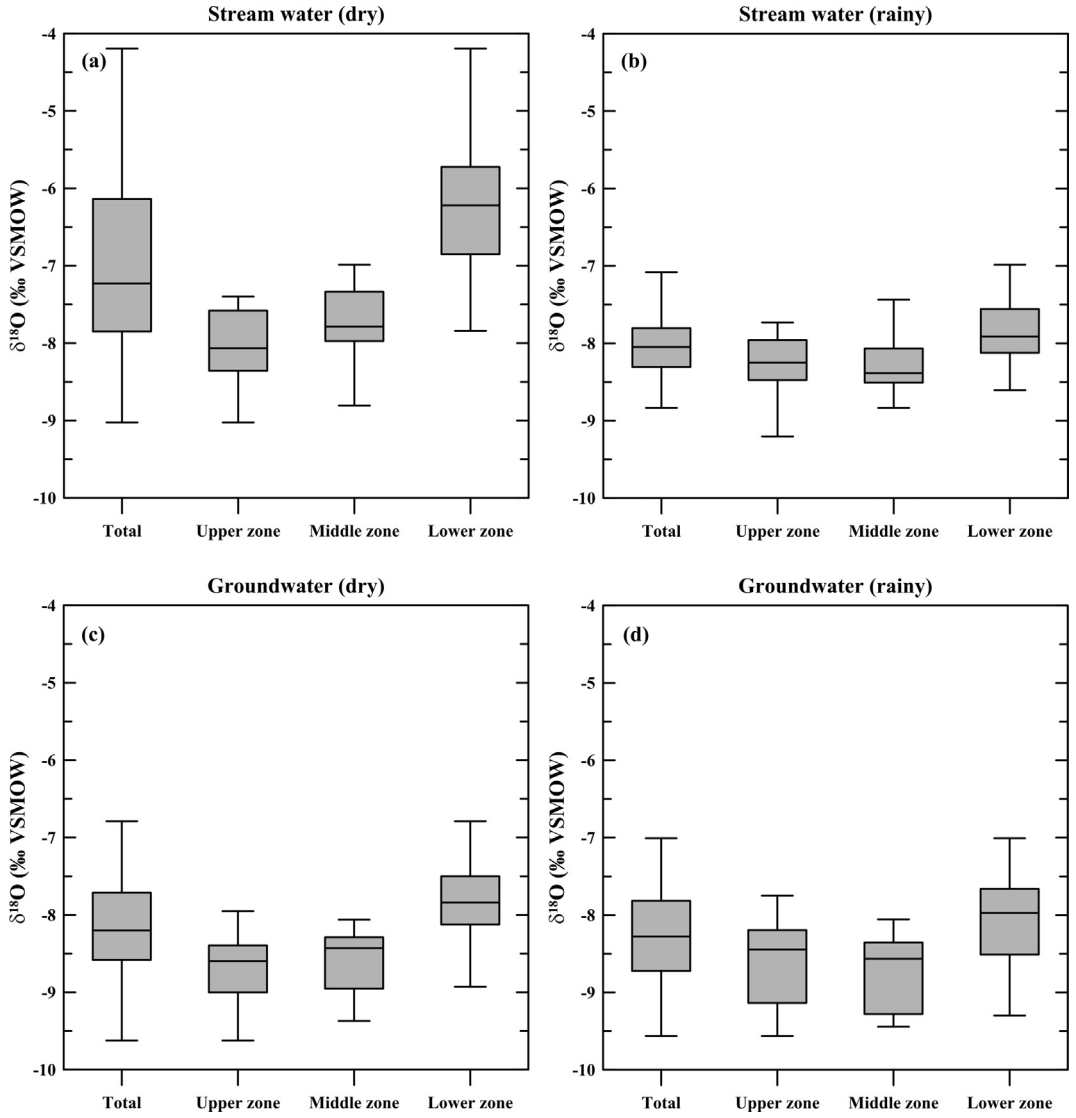

Fig. 5. Box plots of $\delta^{18}O$ for groundwater and stream water in the three hydrographic zones during the dry and wet seasons. The non-outlier range is defined as 1.5 times the interquartile range.

rainy season (Fig. 4(b)).

The stable isotopic composition was more depleted in the upper zone than the lower zone, with that in the middle zones falling between these two groups, but closer to the upper zone (Fig. 5(a)). The spatial differences in $\delta^{18}O$ and $\delta^{2}H$ were significantly reduced in the rainy season compared to the dry season (Figs. 4 and 5(b)). In addition, the range of $\delta^{18}O$ in the plain area during the rainy season was much narrower than that in the dry season. The difference in the median value of $\delta^{18}O$ between the upper zone and lower zone was reduced from 1.8‰ in the dry season to 0.3‰ in the rainy season. The seasonal variation of $\delta^{18}O$ in the upper zone was smaller than in other zones based on the median value and range. In contrast, stream water in the lower zones showed strong seasonality in estimated recharge altitude compared to other zones (Fig. 6).

The seasonal $\delta^{18}O$ and $\delta^{2}H$ values of evaporating water were calculated using Rayleigh distillation with a total fractionation factor according to the equations defined by Majoube (1971) and Gonfiantini (1986). The average annual air temperature and relative humidity over the last 30 years (1981–2010) of Cheonan and Jangsu KMA stations were 11.1 °C and 72.8%, respectively, which were used for the evaporation calculation, and the average $\delta^{18}O$ and $\delta^{2}H$ values of groundwater in the upper zone, −8.6‰ and −58.6‰, were used as the initial values. The seasonal variability of stream water in the lower zone was significantly higher than those of other zones (Fig. 4(c) and (d)). Based on Rayleigh evaporation lines, stream water in the lower zone was affected by 10–20% evaporation in the dry season and 5–10% evaporation in the rainy season (Fig. 4). The evaporation estimate in the rainy season is similar to 7–13% obtained for the Han River basin in Korea during summer season (Ryu et al., 2007).

To identify the sources of stream water in the lower zones, the stream network in the Geum River basin was classified using the Strahler stream order system, and stream water $\delta^{18}O$ was compared in the dry and rainy seasons (Fig. 7). The $\delta^{18}O$ of stream water became enriched with increasing stream order in the upper zones and middle zones regardless of season. However, the $\delta^{18}O$ of stream water became depleted with increasing stream order in the lower zones in the rainy season despite extensive agricultural activities in the area. These isotopic trends indicate that the contribution of stream water originating from the upper zones is high throughout the stream network in the rainy season, which was confirmed by the similarity of the stable isotopic compositions of stream water and groundwater during the rainy season (Fig. 4).

The spatial variations in $\delta^{18}O$ and $\delta^{2}H$ of groundwater indicated more depleted isotopic compositions in the upper zone than the lower

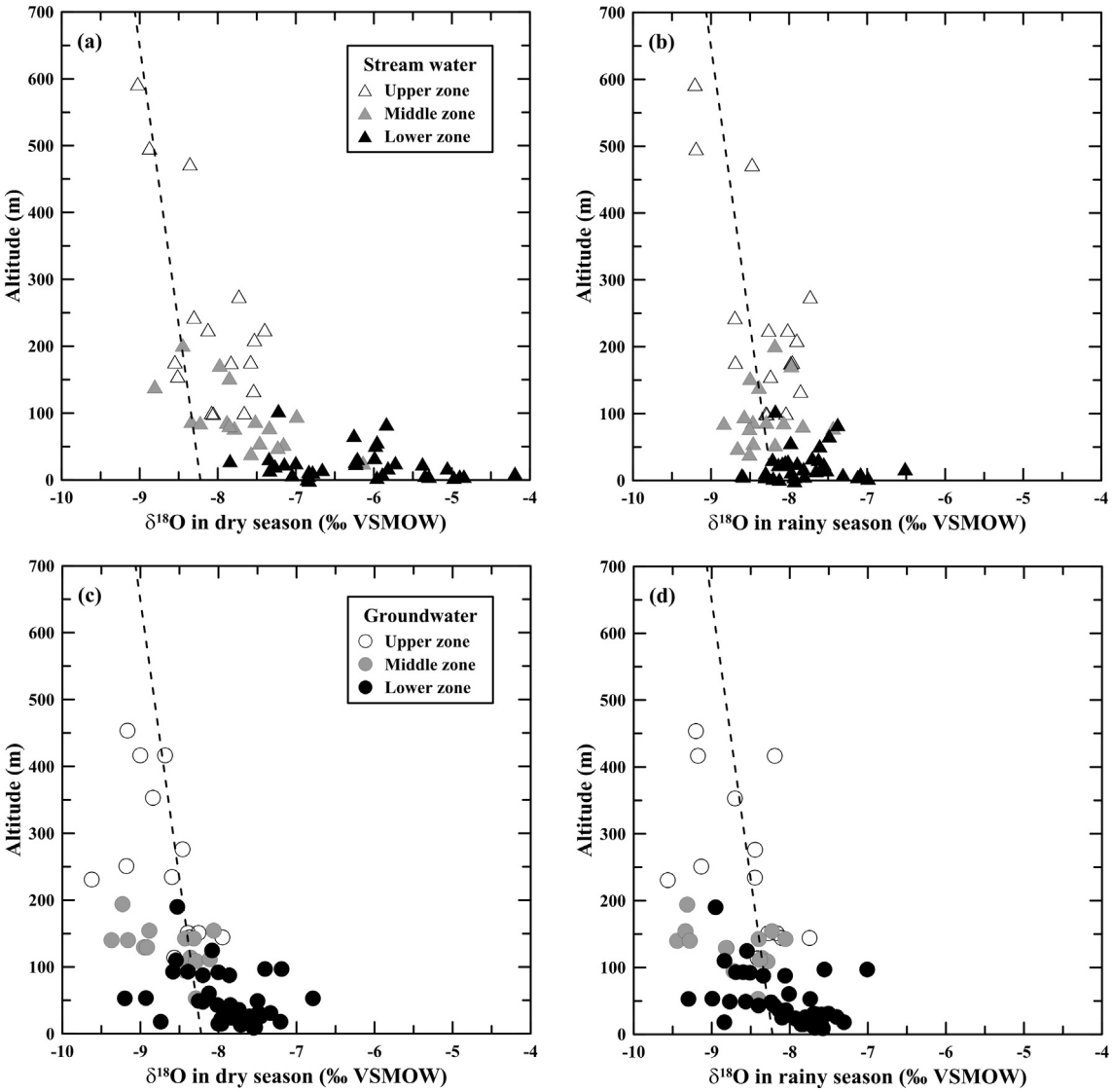

Fig. 6. Stable isotopic compositions versus altitude (m a.m.s.l.) of groundwater and stream water in the dry and rainy seasons. The dashed line denotes the isotopic lapse rate with changing altitude in the study area.

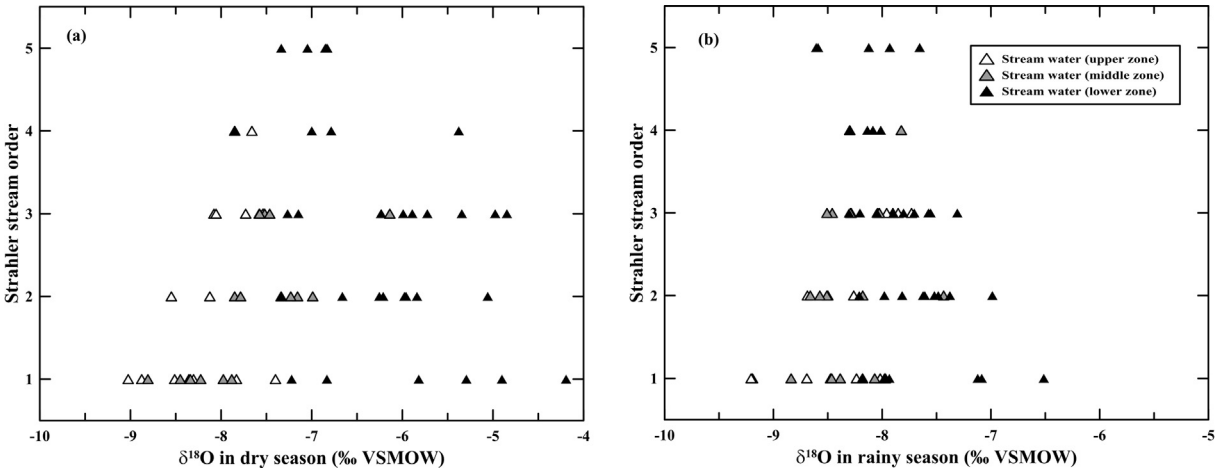

Fig. 7. $\delta^{18}O$ of stream water according to stream order in the Geum River basin for the dry season (a) and rainy season (b). Stream order was classified using the Strahler stream-order number (Strahler, 1957).

Table 4
The amount fraction of rainy season precipitation and its contribution to stream water and groundwater based on deuterium excess in the Geum River basin.

Hydrographic zone	Rainy season amount fraction (%)[1)]	Rainy season contribution (%)[2)]			
		Stream water in dry season	Stream water in rainy season	Groundwater in dry season	Groundwater in rainy season
Upper zone	69	69	74	71	81
Middle zone	71	84	74	81	71
Lower zone	70	–	–	89	81

1) based on climatological normal precipitation from 1981 to 2010 at Jangsu, Daejeon, and Cheonan station of Korea Meteorological Agency for upper, middle, and lower zone, respectively.
2) Calculated using measured deuterium excess values of stream water and groundwater in this study and those of precipitation from 1999 to 2016 at Cheongju GNIP station.

zone, similar to those of stream water (Fig. 4). The average values of stable isotopic composition in groundwater were relatively constant in two seasons (Fig. 5), indicating that the groundwater flow system was stable in the basin as a whole. However, the ranges of isotopic composition showed considerable variations between the two seasons, suggesting that some aquifers had local recharge with higher seasonal variability.

The relative contribution of precipitation to total recharge in dry and rainy seasons was calculated based on two-component mixing using average *d* values in precipitation of the two seasons. (Winograd et al., 1998; Lee et al., 1999). The representative d values of precipitation were estimated from the measurements at Cheongju GNIP station from 1999 to 2016 as 16.2‰ and 8.3‰ for dry and rainy season, respectively. Compared with precipitation amount of rainy season as a fraction of total precipitation of 69–71% over the last 30 years, the contribution of rainy season precipitation to groundwater recharge was disproportionately dominant, accounting for 71–89% while the contribution of rainy season precipitation to surface water was similar to the amount fractions except the middle zone in dry season (Table 4). The predominance of rainy season precipitation to groundwater recharge was most pronounced in the lower zone in dry season.

4.3. Reconstructed ^3H input and groundwater ^3H

To estimate residence time of groundwater from measured ^3H, the ^3H input history of the Geum River basin was reconstructed. Koh and Chae (2008) reconstructed the ^3H input history in Daejeon from 1950 to 2000 using ^3H measurement data at 11 GNIP stations in the Northern Hemisphere and 3 GNIP stations in South Korea. In this study, ^3H input from precipitation was extended to the period between 2001 and 2015 using monthly ^3H measurements for precipitation at the Daejeon station of the Korea Institute of Nuclear Safety, which were weighted based on monthly precipitation. The two series of ^3H inputs matched well, without significant discontinuity in temporal trends (Fig. 8).

Based on the reconstructed ^3H values in precipitation, groundwater recharged before 1950 contained ^3H below 0.5 TU, while young groundwater with recent recharge contained ^3H ranging from 2 to 6 TU. The effect of bomb ^3H was assumed to be negligible for most groundwater samples because the ^3H peak is highly likely to be dispersed and mixed in aquifers if there is no significant lag in the thick unsaturated zone. ^3H concentrations ranging from 0.5 to 2 TU can be regarded as mixtures of ^3H-free old water and young groundwater. In this study, qualitative groundwater ages using ^3H concentration were used to designate samples as old groundwater with ^3H less than 0.5 TU, young groundwater with ^3H greater than 2 TU, and mixed groundwater with ^3H from 0.5 TU to 2 TU. This approach has been previously applied to volcanic aquifers on Jeju Island, Korea (Koh et al., 2005).

The ^3H concentration in groundwater in the study area ranged from 0.3 to 5.4 TU (Table 5). The median ^3H concentration was 2.8 TU in shallow groundwater and 2.2 TU in bedrock groundwater, which did not differ significantly (p-value = 0.22, *t*-test) (Fig. 9(a)). In shallow groundwater, 19% of samples corresponded to mixed groundwater and 81% to young groundwater. In bedrock groundwater, 11% corresponded to old groundwater, 35% to mixed groundwater, and 54% to young groundwater. The ^3H concentrations in groundwater were clearly distinguished among hydrographic zones. Groundwater in the

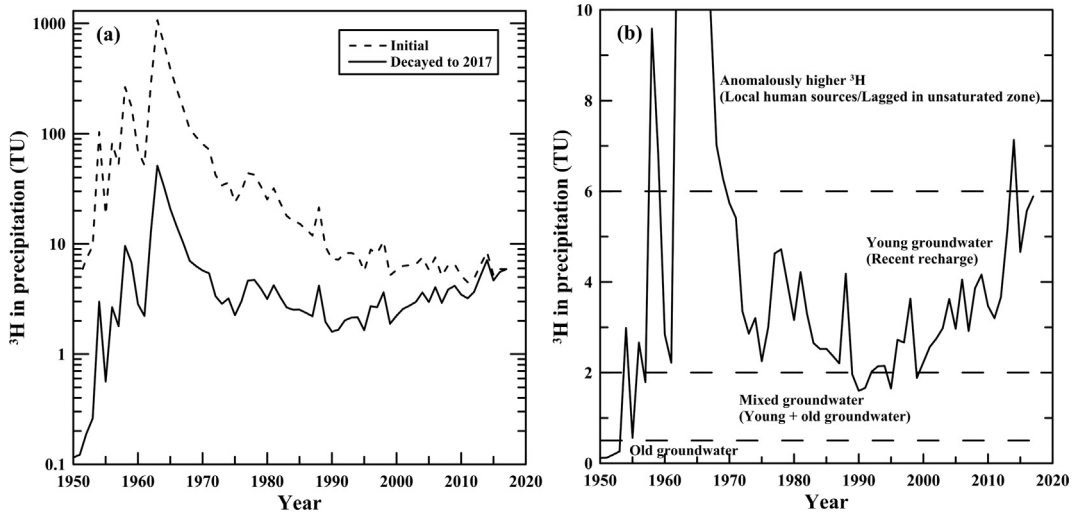

Fig. 8. Reconstructed ^3H input history in Daejeon based on ^3H input histories from Koh and Chae (2008) and measurements in Daejeon from annual reports on environmental radioactivity by the Korea Institute of Nuclear Safety from 2001 to 2015. ^3H levels of 0.5–2 TU were assumed to result from mixing of ^3H-free old groundwater and young groundwater recharged since the 1950s based on the reconstructed ^3H input history.

Table 5
Measured tritium concentration (TU) of groundwater in dry season.

Hydrographic zone	n	Minimum	Maximum	Average	Standard deviation
Total	67	0.3	5.4	2.5	1.27
Upper zone	13	0.3	4.1	2.0	0.95
Middle zone	14	0.3	4.7	2.0	1.30
Lower zone	40	0.3	5.4	2.9	1.23

upper zone showed a significant difference from that in the lower zone (p-value < 0.01, *t*-test). Groundwater in the middle zone had a median ^{3}H value similar to the upper zone, but a wider range (Fig. 9(b)).

4.4. End-member mixing analysis of environmental isotopes

The EMMA approach based on the mass balance of tracers has been widely used for hydrograph separation (Burns et al., 2001; Maurya et al., 2011). Previous studies have used the $\delta^{18}O$ and $\delta^{2}H$ values of water with Cl^{-} concentration or EC to distinguish sources and flow paths in groundwater systems (Nakaya et al., 2007; Peng et al., 2018; Rey et al., 2018). Cl^{-} is a conservative tracer that can be used to evaluate groundwater recharge in alluvial sediments (Subyani, 2004; Liu and Yamanaka, 2012). EC is also a useful tracer, and can be used to identify seawater intrusion effects or differences in water–rock interactions depending on aquifer type.

In the study area, mountainous terrain acts as water storage; therefore, understanding the hydrological processes in the mountainous area is important for maintaining water resources in the adjacent plain area (Viviroli et al., 2007; Peng et al., 2018). Recently, groundwater recharge in the mountainous area has been determined to significantly contribute to regional groundwater and streamflow systems (Tetzlaff and Soulsby, 2008; Ajami et al., 2011). Previous studies have identified the process of mountain system recharge (MSR) as the main source of water to plain areas (Anderson et al., 1992; Viviroli and Weingarther, 2004; Wilson and Guan, 2004; Liu and Yamanaka, 2012; Peng et al., 2018).

We tried to determine the relative importance of MSR and surface water–groundwater interactions using EMMA for $\delta^{18}O$ and $\delta^{2}H$ in groundwater and stream water. Cl^{-} concentration and EC were also considered, but could not easily distinguish end-members associated with sources of water and flow paths. These tracers can be affected in various ways depending on lithology and land-use patterns, distribution of contamination sources, and the influence of seawater in coastal areas (Peng et al., 2016; Shin et al., 2017). In this regard, EMMA using $\delta^{18}O$ and *d* value, and ^{3}H in groundwater was employed to clarify the contributions of groundwater flow in mountainous areas and surface-groundwater interaction in the Geum River basin. Few studies have applied $\delta^{18}O$ and *d* value for evaluation of evaporation effects and groundwater mixing processes (Tsujimura et al., 2007; Joshi et al., 2018). Three end-members were assigned using the amount-weighted average values of summer precipitation (end-member A), winter precipitation (end-member B), and evaporated stream water (end-member C) in plain areas. Most groundwater and stream water samples fell within the triangle made by these end-members (Fig. 10), indicating that the end-member system could account for the majority of variance in the stable isotopic composition of water samples. Therefore, these three end-members represented the seasonal variability in groundwater recharge and the surface water flow system associated with the hydroclimatic conditions of rainfall, snowfall and evaporation, as well as the degree of surface water–groundwater interaction.

EMMA of environmental tracers revealed distinct spatial and temporal patterns of the relative contributions of recharge sources in the study area. Each end-member was characteristic of a distinct group of water samples. Groundwater with high fraction of end-member A had the lowest ^{3}H concentration, representing the contribution to regional flow from summer precipitation. Meanwhile, groundwater in the lower zone had higher ^{3}H values, indicating the dominance of local recharge, in accordance with the more enriched isotopic composition of groundwater in that area. Some stream water samples collected in the upper zone had higher fractions of end-member B, which is generally attributed to winter precipitation. End-member C mainly contributed to stream water in the lower zone, where local recharge, including that of evaporated water, is most likely to discharge into streams.

The relative contributions of three end members to groundwater and stream water showed clear differences according to the three hydrographic zones (Fig. 11). A considerable portion of stream water sampled in the upper zones and the middle zones overlapped with groundwater in the EMMA of stable isotopes (Fig. 10), indicating that groundwater from mountainous terrain is the main source of stream water in these areas. Other stream water samples away from groundwater appear to be affected by rapid infiltration of precipitation, leading to seasonal variability of isotopic composition.

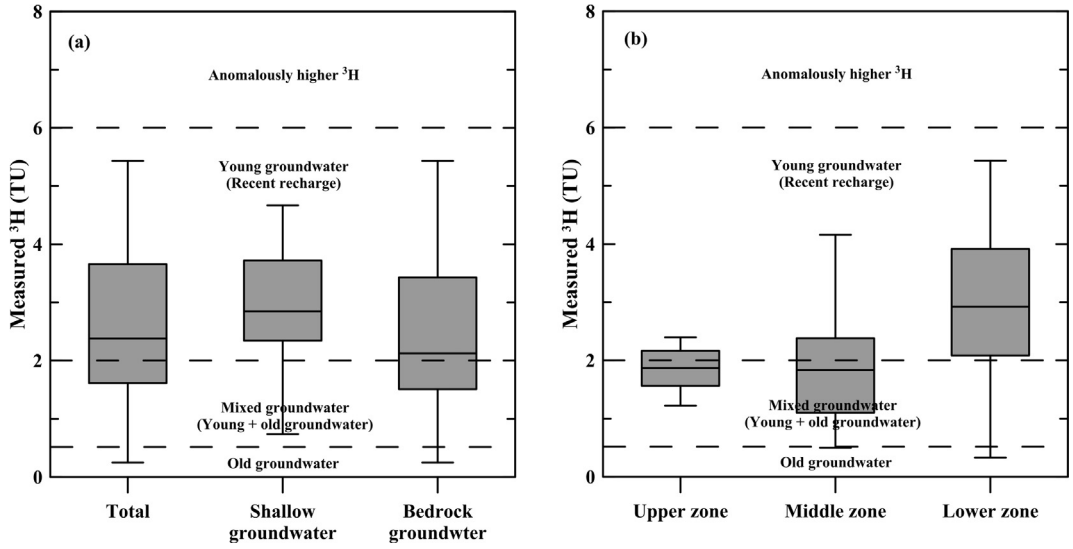

Fig. 9. ^{3}H concentration in groundwater for aquifer types (a) and hydrographic zones (b). The non-outlier range is defined as 1.5 times the interquartile range.

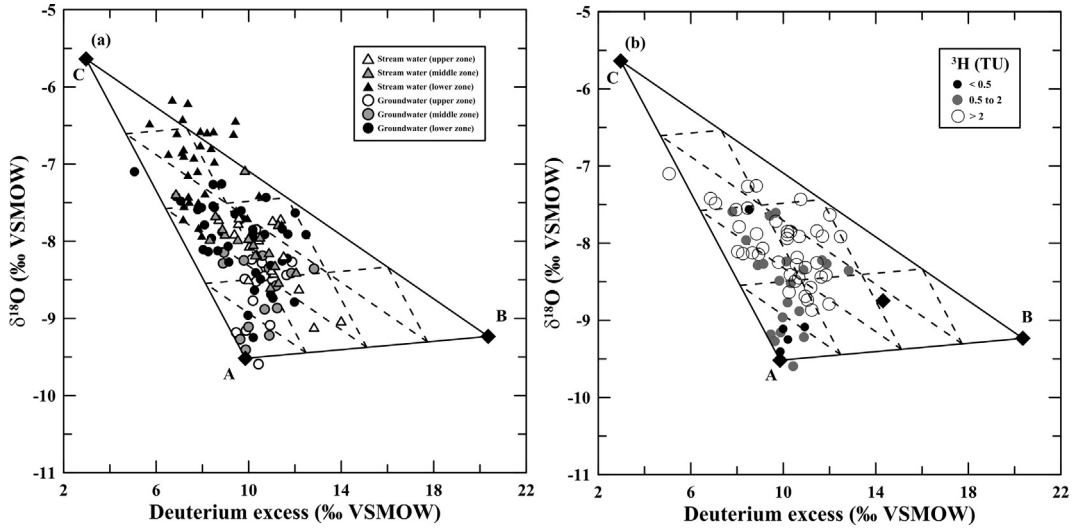

Fig. 10. Deuterium excess versus $\delta^{18}O$ of groundwater and stream water in the dry season (a) and that of groundwater, showing age groups based on ^{3}H (b). Dashed lines represent mixing lines between the three end-members at 25% intervals.

5. Discussion

5.1. Water sources and flow processes in the basin

The depleted isotopic compositions of stream water in the upper zone with less seasonal variability can be attributed to the significant contribution of groundwater inflow from adjacent mountainous terrains, where orographic lift enhances the amount of precipitation at higher altitudes, resulting in accelerated precipitation infiltration with depleted $\delta^{18}O$ and $\delta^{2}H$ (Tappa et al., 2016). Choi et al. (2007) and Combalicer et al. (2008) reported recharge rate higher than 21% in mountainous areas in Korea, which is significantly higher than average recharge rate of 14% in the Geum River basin. Previous studies in the Mt. Gyeryong region of the Geum River basin showed that groundwater significantly contributed to discharge in headwater streams in the mountainous region with a thin soil layer based on antecedent precipitation index models (Jung et al., 2016). These results indicate that active groundwater discharge to streams may occur in the study area due to the hydrologic features of its mountainous terrain corroborating that first-order streams in mountainous terrains play significant roles in maintaining stream discharge for the whole stream network (Alexander et al., 2007; Nadeau and Rains, 2007). Tezlaff and Soulsby (2008) also reported that mountainous catchments can make an important contribution to downstream flows although mountainous regions underlain by crystalline aquifers with thin soil have limited aquifer potential and groundwater storage.

The more enriched isotopic composition of stream water in the lower zones with greater seasonal variability could be attributed to the seasonally variable effect of evaporation and less influence of MSR at higher altitudes, which was more pronounced in the dry season (Fig. 6). These observations indicate that streams in the lower zone are controlled by seasonally variable and presumably more local flow systems. In the lower zones, the land use of most areas near the stream consists of rice paddies, where impounded water affected by evaporation contributes to stream discharge as base flow (Todd et al., 2006) or return flow (Koh et al., 2010; Negrel et al., 2011). Conversely, during the rainy season, the increased groundwater contribution from mountainous terrains maintains a higher stream water level than the groundwater in adjacent aquifers (Gabrielli et al., 2012), decreasing the inflow of impounded water (Buttle et al., 2012). Stream water impounded by various storage facilities in the basin for water use may be evaporated to a considerable degree in dry season, which also contribute to evaporation signature in stable isotopic composition (Simpson and Herczeg 1991; Ryu et al., 2007; Vanplantinga et al., 2017). These features shows that anthropogenic activities significantly affect sources and processes of streamflow in the lower zone of the Geum River basin.

The stable isotopic composition of groundwater was close to the LMWL in summer, and fairly stable regardless of season (Fig. 4). The *d* value of groundwater exhibited minor seasonal differences of less than 1‰. Considering the highly variable *d* value of seasonal precipitation due to changing water vapor sources, these results suggest that groundwater is mainly recharged through rainy season precipitation. Among seasonal sources of groundwater recharge in areas with thick soil layers and heavy vegetation, many studies have emphasized the importance of snow pack and precipitation in winter due to increased evapotranspiration in summer (Wassenaar, 1995; Winograd et al., 1998; Blasch and Bryson, 2007; Rey et al., 2018). In contrast, some studies in Asian monsoon regions have reported the dominance of rainy season precipitation in groundwater recharge, accounting for 66–71% in various regions of Korea (Lee et al., 1999; Lee and Kim 2007; Gautam et al., 2018) and 75.5% in Taiwan (Yeh et al., 2014), which are similar or lower than the fractions of rainy season precipitation in total precipitation. In this study, the contribution of rainy season precipitation to recharge was 82–91% excluding that in the lower zone sampled in dry season which can be affected by evaporation, and was higher than the amount fraction in precipitation (Table 4), in contrast to the results of previous studies. This finding suggests a weak contribution of precipitation in winter, including through snow melt in early spring, and highly efficient recharge from summer precipitation due to reduced evapotranspiration compared to areas without monsoon seasons.

A considerable portion of groundwater in the upper zones and the middle zones had depleted $\delta^{18}O$ values due to recharge from high-altitude areas (Figs. 5 and 6). In addition, the lower ^{3}H of groundwater in bedrock aquifers in those areas indicates that groundwater flow through longer flow paths plays a key role in recharging the aquifers, because tectonic structures such as dense sub-horizontal and sub-vertical fractures create major flow paths in crystalline bedrock aquifers (Taylor and Howard, 2000; Dewandel et al., 2006; Pacheco, 2015). Meanwhile, in the lower zones, seasonal variations in the isotopic composition and ^{3}H concentration of groundwater were greater than those in other zones. Seasonally, some groundwater had more depleted stable isotopic composition in rainy season compared to that in dry season due to fast infiltration of depleted heavy rainfall, whose proportion is 8%, 57%, and 72% for the upper, middle, and lower zones, respectively. This indicates that local groundwater flow is more active in the well-developed permeable alluvial layers of the lower zone in

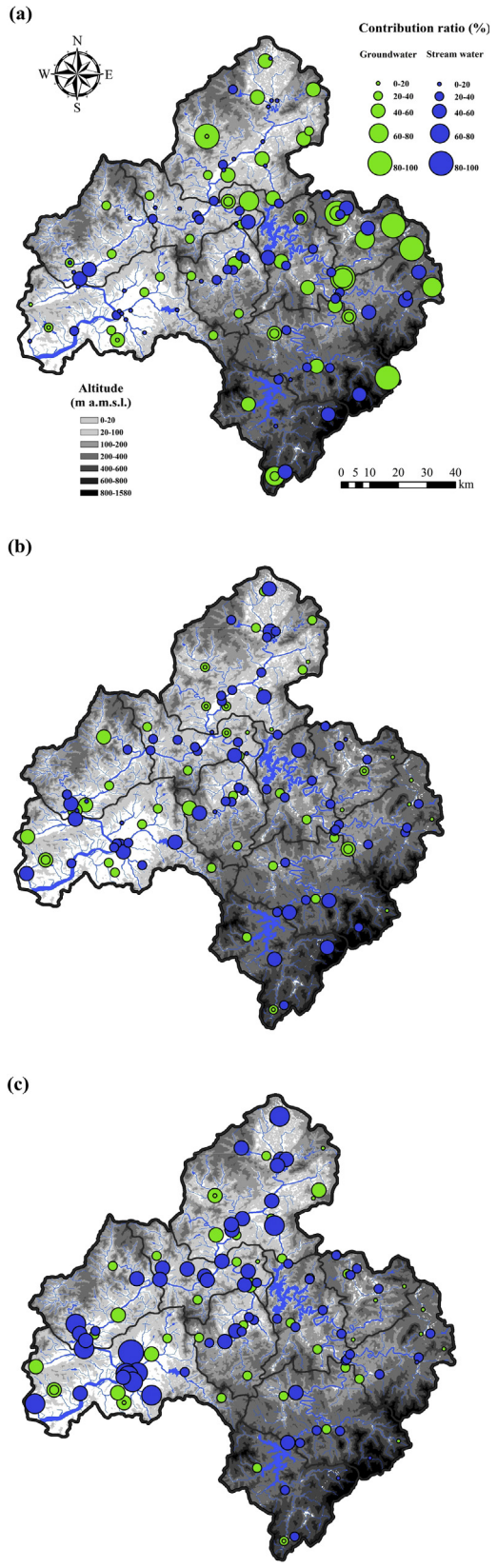

Fig. 11. Spatial distributions of the relative contributions of the three end-members to groundwater and stream water for rainy season precipitation (a), dry season precipitation (b), and local recharge including evaporated water (c).

rainy season. In agricultural areas near streams in Korea, impounded water in paddy fields during growing season has strong evaporation signature and can infiltrate to the aquifers below. In some riparian areas, the large gradient in groundwater level caused by pumping induces inflow from adjacent streams (Kwon et al., 2017). For these reasons, groundwater in the lower zones is highly likely to have multiple sources of recharge, resulting in a wide range of stable isotopic compositions and ^{3}H contents.

5.2. Stream water and groundwater flow systems and their implications

Stable isotopic compositions of groundwater samples indicate that higher altitude recharge in the upper zone seem to be less significant to the lower zone while the middle zone may have a certain amount of recharge from the upper zone (Fig. 5). ^{3}H concentration in groundwater indicates that young water predominate in the lower zone and old water significantly contributes to the upper and middle zones (Fig. 9). The EMMA results showed an intermediate recharge process with long flow paths originating from mountainous terrains was dominant for groundwater in the upper zones, whereas the contribution of local recharge and stream–aquifer interactions to groundwater increased toward the lower zones (Fig. 10). Based on these isotopic signatures in the three hydrographic zones, regional groundwater flow across the basin appears to be insignificant while intermediate groundwater flow between the upper zone and the middle zone can be significant.

Groundwater and stream water in the lower zones were widely separated in terms of the contributions of the three end-members (Fig. 10). A permeable sandy point-bar is generally developed around higher-order streams in the plain area due to the absence of impermeable silty soil (Chae et al., 2004). Considering these alluvial strata, lateral flow through the sandy layer in plain area may be the dominant flow path supplying evaporated water to streams in the dry season. Meanwhile, the depth of the sandy alluvium strata decreases and impermeable mud and silty layers are frequently observed further from stream channels in the plain area (Choi et al., 2010). In the rainy season, streams under losing conditions appear to affect adjacent groundwater in the lower zones based on the higher estimated recharge altitude and elevated ^{3}H in groundwater.

We constructed a conceptual model for groundwater flow systems involving local and intermediate flows, and streamflow generation sustained by the groundwater flows for the Geum River basin for the two representative seasons integrating the results of environmental isotopes in groundwater and stream water (Fig. 12). This model highlights that groundwater flow systems are spatially different and seasonally less variable in the three hydrographic zones while streamflow from groundwater is seasonally highly variable with higher contribution from mountainous terrains to the whole stream network in rainy season. In some previous studies, the groundwater flow systems in the basin were constructed based on compilation of fractured zones and faults of the basin (Pacheco and Van der Weijden, 2014a; Pacheco, 2015). However, these data are not available for the basin at present, which suggests more research is necessary to understand the groundwater flow systems of the basin, in particular, regional groundwater flow.

On the Korean Peninsula, the intensity and frequency of extreme summer precipitation is expected increase in the near future (2021–2100) compared with the present, and the number of non-precipitation days during spring and summer are also expected to rise based on regional climate models (Kim et al., 2018). In the study area, amount of precipitation, days of heavy rainfall, and precipitation intensity in the study area are expected to increase by 22.4 mm/10 years, 12.94%/10 years, and 1.71%/10 years from 2011 to 2100, respectively, according to the RCP8.5 scenario in the Geum River basin area (KMA, 2012). These changes in precipitation patterns due to climate change may have considerable impacts on groundwater and surface water flow systems, as our results indicate a disproportionately large role of

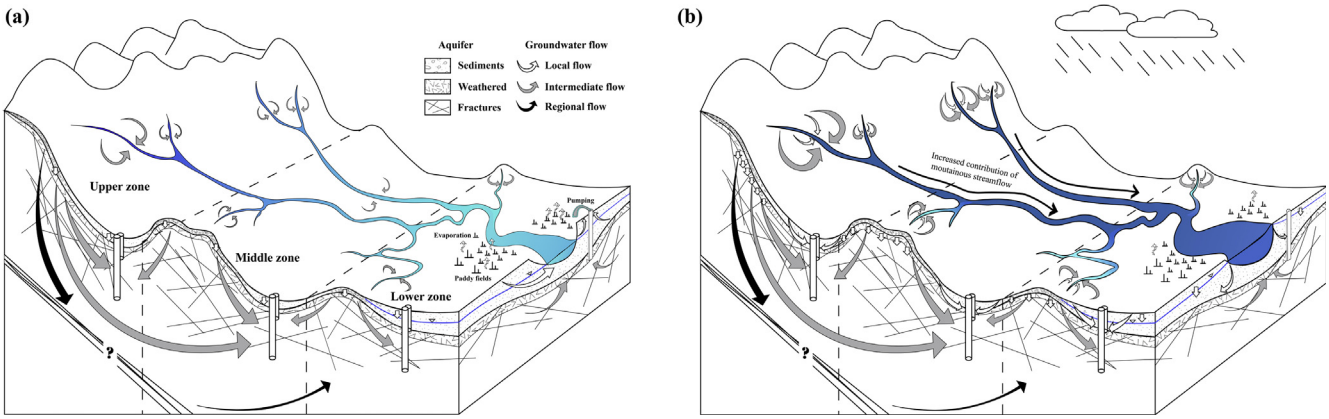

Fig. 12. Conceptual model for groundwater flow systems and their relationship with streamflow of the Geum River Basin based on stable isotopes and tritium in dry season (a) and rainy season (b).

summer precipitation in the water resources in the study area. The maximum shortage rate of water for agricultural use will be 38% for the 2040 s in the Geum River basin under the RCP 4.5 scenario and an obvious decrease in water shortage was expected to be common in June, whereas the water stress was expected to intensify in August, because of the increased variability in future climate (Ahn et al., 2016). The sensitivity of streamflow in the upper zone of the Geum River basin to timing shift of the monsoon season was also shown by hydrologic modeling using future climate change scenarios (Ryu et al., 2011). In terms of the hydrographic zones of the Geum River basin, the impact of climate change is likely to affect the lower zone on a short-term scale and other zones on a longer term due to different groundwater flow systems, and streamflow to be highly sensitive to changes in groundwater discharge in the mountainous terrain comprising the upper and middle zones (Fig. 12). This research may provide important information for sustainable management of water resources in the Geum River basin and will serve as a prototype to assess stream and groundwater flow systems in other regions with similar climatic and hydrologic conditions.

6. Conclusions

Stable isotopes and ^{3}H in groundwater and stream water in the Geum River basin showed spatial and temporal variations depending on the three hydrographic zones of upper, middle, and lower zones, and these trends were compared with the stable isotopes in precipitation in the basin. Groundwater derived from rainy season precipitation was significantly higher than amount fractions of rainy season precipitation in total precipitation indicating the minor role of dry season precipitation, including snow melt, in recharge. The stable isotopic compositions of groundwater and stream water in the upper and middle zones were fairly constant throughout the dry and rainy seasons, and most groundwater and stream water were derived from high-altitude areas based on the altitude effect on $\delta^{18}O$. This indicates that groundwater recharge from mountainous terrains is the main source of streamflow and groundwater flow in the upper and middle zones. In contrast, groundwater in the lower zone exhibited some seasonal variabilities of its stable isotopic composition as well as changes in recharge altitude in some groundwater samples. An evaporation signature of stable isotopes was considerable in groundwater and stream water of the lower zone, which was more pronounced in the dry season. The $\delta^{18}O$ values of stream water became more depleted with increasing stream order in the lower zone, approaching those in the upper zone, which indicated that groundwater discharge in the mountainous areas contributed considerably to the discharge of the main stream of the Geum River. The relative contributions of rainy season precipitation, dry season precipitation, and local recharge with evaporation signature were quantified using $\delta^{18}O$ and *d* value along with ^{3}H in groundwater. Rainy season precipitation was dominant in the groundwater of the upper zone, while local recharge affected by evaporation was the greatest contributor to stream water in the lower zone. ^{3}H in groundwater indicated that intermediate recharge with longer flow paths originating from the mountainous areas was a dominant factor affecting groundwater in the upper zone, but its contribution decreased toward the lower zone. These results contribute to understanding the water sources and hydrologic processes of the groundwater and stream water systems in the Geum River basin and promote sustainable management of water resources at the regional scale considering future changes in water use and precipitation patterns due to climate change.

Declaration of interests

None.

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